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(54) GELLED AQUEOUS INORGANIC ACID SOLUTIONS AND METHODS OF USING THE SAME

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SEP 22 1981 Abstract of the Disclosure 1109356

Gelled aqueous inorganic acid solutions and methods of treating subterranean well formations using such solutions comprising water, at least one water soluble inorganic acid and a gelling agent comprised of a solution of a water soluble organic solvent and an ethoxylated fatty amine or a mixture of such amines.

Acidizing and fracturing procedures using aqueous acid solutions are commonly carried out in subterranean well formations to accomplish a number of purposes, one of which is to facilitate the increase in the recovery of hydrocarbons therefrom. In acidizing procedures, aqueous acid solutions are introduced into well formations under pressure so that the acid solutions flow into the pore spaces of the formations and react with materials contained therein whereby the pore spaces are enlarged and the permeability of the formations increased. In fracture acidizing procedures, one or more fractures are produced in the formations and the acid solutions are introduced into the fractures to etch flow channels therein and/or to enlarge the pore spaces in the fracture faces and in the formations.

Increasing the viscosity of an aqueous acid solution, hereinafter referred to as "gelling," by the inclusion of certain swellable materials or gelling agents therein has been accomplished heretofore. In acidizing and/or fracture acidizing subterranean formations, gelled aqueous acid solutions are useful in preventing the acid from becoming prematurely spent and inactive. In addition, gelling of the acid solutions enables the development of wider fractures so that live acid can be forced further into the formation from the well bore. Furthermore, increasing the

viscosities of the acid solutions also permits better fluid loss control.

Gelled aqueous acid solutions have utility in industrial applications other than in the treatment of subterranean well formations such as in the cleaning of industrial equipment.

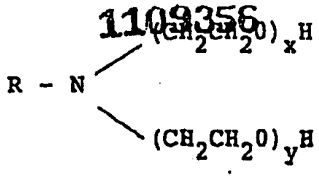
Gelling agents such as hydratable gums and cellulose derivatives have been utilized to increase the viscosity of aqueous acid solutions. However, the gels produced using such gelling agents generally have limited stability at high temperatures in the presence of acid. Other gelling agents which increase the viscosity of aqueous acid solutions have been developed and used, but they are often difficult to disperse and usually require considerable mixing or agitation to develop full viscosity. Still other prior art gelling agents can form an undesirable precipitate during the dissolution of formation materials such as limestone or dolomite, which precipitate can remain in the formation to thereby damage it by decreasing the permeability thereof.

By the present invention, a gelling agent for increasing the viscosity of aqueous acid solutions, the resulting gelled aqueous acid solutions and methods of using such gelled aqueous acid solutions are provided. The gelling agent of the present invention can be easily dispersed into

an aqueous acid solution and only a small quantity of it is required to rapidly increase the viscosity of the acid solution with a minimum of mixing and agitation. The resulting gelled aqueous acid solutions of the present invention have excellent stability over a broad temperature range; they are relatively non-damaging to subterranean formations treated therewith; and, upon becoming spent in subterranean formations, and, without the inclusion of chemical breakers or special additives therein, they break to low viscosity liquids having excellent fines suspension properties.

The present invention relates to a gelled aqueous inorganic acid solution comprising water, at least one water soluble inorganic acid and a gelling agent, said gelling agent being comprised of a water soluble organic solvent selected from the group consisting of alkanols having in the range of from about 1 to 5 carbon atoms per molecule, ketones having in the range of about 3 to 6 carbon atoms per molecule, polyhydroxy compounds having in the range of about 2 to 6 carbon atoms per molecule, ethers having in the range of about 2 to 6 carbon atoms per molecule, compounds containing both ether and alcohol functions having in the range of about 4 to 8 carbon atoms per molecule, esters having in the range of about 2 to 6 carbon atoms per molecule, lactones having in the range of about 3 to 5 carbon atoms per molecule and mixtures of two or more of the foregoing compounds, and a mixture of ethoxylated fatty amines dissolved in said water soluble organic solvent having the general formula:

A



(1)

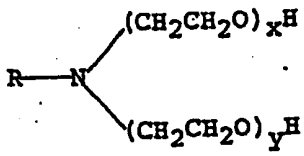
wherein:

R is selected from saturated and unsaturated aliphatic groups having in the range of from about 8 to about 22 carbon atoms, and mixtures thereof, and x and y each have a value in the range of from about 0 to about 10. The preferred ethoxylated fatty amines and mixtures thereof useful herein are those wherein the average sum of the values of x and y in the amines used is in the range of from about 1.8 to about 2.2.

A

Mixtures of ethoxylated tertiary fatty amines derived from fats and oils such as coconut oil, soy bean oil, and tallow are particularly suitable for use in accordance with the present invention.

A preferred mixture of ethoxylated fatty amines for use in this invention is a mixture of amines of the general formula:



(2)

wherein:

R is selected from the group consisting of saturated and unsaturated aliphatic groups having in the range of from about 14 to about 18 carbon atoms and mixtures of such groups; and

wherein the average sum of the values of x and y in the mixture of ethoxylated amines is equal to 2.

In the most preferred embodiment, x and y each have a value of 1 (one).

Examples of such amines are those derived from fatty acids of the type hexadecyl, tallow, soya and oleyl, either saturated or unsaturated and either as pure components or mixtures.

A variety of organic solvents can be utilized in making the gelling agents so long as such solvents are capable

of dissolving the ethoxylated fatty amines and are also water soluble. Examples of such water soluble organic solvents include alkanols having in the range of about 1 to 5 carbon atoms per molecule, such as methanol, ethanol, isopropanol and t-butanol; ketones having in the range of about 3 to 6 carbon atoms per molecule, such as acetone and methylethyl ketone; polyhydroxy compounds having in the range of about 2 to 6 carbon atoms per molecule, such as ethylene glycol and glycerine; ethers having in the range of about 2 to 6 carbon atoms per molecule, such as dioxane and tetrahydrofuran; compounds containing both ether and alcohol functions having in the range of about 4 to 8 carbon atoms per molecule, such as diethylene glycol and triethylene glycol; organic acids having in the range of about 1 to 10 carbon atoms per molecule, such as formic acid, malonic acid, acetic acid, gluconic acid, levulinic acid and propionic acid; esters having in the range of about 2 to 6 carbon atoms per molecule, such as methyl formate, dimethyl oxylate and dimethyl malonate; and lactones having in the range of about 3 to 5 carbon atoms per molecule, such as beta-propyl lactone and gamma-butyl lactone. Due to the desirably low freezing point and/or high flash point (tag closed cup) of the resulting gelling agent the organic acids are preferred with acetic acid being the most preferred.

The water soluble organic solvent useful herein is

preferably in liquid phase at the temperature at which it is mixed with the ethoxylated fatty amine. Furthermore, mixtures of the organic solvents can be used. An example is a mixture of methanol and gluconic acid.

The gelling agents useful herein can be prepared by mixing the water soluble organic solvents with the ethoxylated fatty amines for a period of time sufficient to completely dissolve the amines in the solvents. The quantity of ethoxylated amines dissolved in the organic solvent range in an amount of from about 10 to about 80, preferably from about 50 to about 60 percent amine by weight of the gelling agent.

As mentioned above, the organic solvents can be used singly, or in mixtures of solvents of the same chemical class (acids with acids, ketones with ketones and the like) or in mixtures of solvents of different chemical classes (acids with alcohols, ethers with ketones and the like). A preferred organic solvent is a mixture of chemicals of different chemical classes wherein at least one of the classes is an organic acid.

The ethoxylated fatty amines useful herein are very difficult to dissolve directly in aqueous inorganic acid solutions. However, the gelling agent of this invention, comprising a solution of the amines dissolved in a water soluble organic solvent, such as acetic acid, readily dissolves in an aqueous inorganic acid solution and substantially immediately increases the viscosity of the acid solution.

The gelling agents of th present invention cause an

increase in the viscosity of aqueous inorganic acid solutions having acid concentrations in the range from about 1 to about 25 percent active acid by weight of the solutions. However, acid solutions having acid concentrations of greater than about 25 percent can be mixed with the gelling agents of this invention and such acid solutions, upon being reacted, will begin to exhibit a noticeable increase in viscosity when the acid concentration, due to the reaction, is diminished to a value of about 25 percent. Such increase in viscosity continues with continued decrease in acid concentration until the acid concentration reaches a value in the range of from about 10 percent to about 15 percent. To this extent then, this invention features a delayed gelling characteristic.

The gelling agents of this invention will cause the viscosity of aqueous inorganic acid solutions having acid concentrations in the range of from about 1 to about 10 percent, and more particularly in the range of from about 1 to about 5 percent, to rapidly increase providing that the presence of dissolved salts in the acid solution is very low and preferably absent. In this connection, the presence of dissolved salts in the gelled acids of this invention cause the gels to break when the acid concentration is less than about 10 percent and particularly when the acid concentration is less than about 5 percent. This breaking feature, as will

be further explained below, can be of particular value when the acid gels of this invention are used to acid treat subterranean formations.

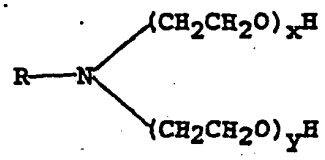
The gelling agents are particularly useful in increasing the viscosity of aqueous inorganic acid solutions such as hydrochloric acid solutions, sulfuric acid solutions, phosphoric acid solutions, hydrofluoric acid solutions and solutions containing mixtures of such acids.

In preparing a gelled aqueous acid solution of this invention, the acid or mixture of acids utilized can be, and is preferably, diluted with water to obtain an aqueous inorganic acid solution of desired acid concentration. A gelling agent of the present invention, i.e., an ethoxylated fatty amine or mixture of such amines of the type described above dissolved in a water soluble organic solvent, is preferably combined with the aqueous acid solution in an amount in the range of from about 0.1 to about 10, and more preferably in the range of from about 2 to 6, percent gelling agent by weight of the aqueous acid solution. The acid solution and gelling agent are agitated or mixed for a short period of time whereupon the viscosity of the aqueous acid solution is increased. More specifically, some increase in viscosity is obtained when as little as 0.1 percent gelling agent is combined with the aqueous acid solution, and greater amounts of the gelling agent bring about increased

viscosity. When the gelling agent is combined with the aqueous acid solution in an amount of about 10 percent by weight of the solution, viscosities of about 150 centipoises can be obtained.

Greater viscosity increase can be obtained through use of gelling agent amounts in excess of 10 percent. Thus, 10 percent is not a limit on the capability of the gelling agent to increase the viscosity of acid, but is viewed as a working guide in view of current process economics and the practical capabilities of currently known liquid handling and pumping equipment.

A gelled aqueous acid solution of this invention is comprised of water, a water soluble inorganic acid or mixture of such acids, and a gelling agent comprised of a solution of a water soluble organic solvent and an ethoxylated fatty amine having the general formula:



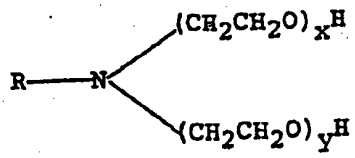
(3)

wherein:

R is selected from saturated and unsaturated aliphatic groups having in the range of from about 8 to about 22 carbon atoms, and mixtures thereof, and x and y each have a value in the range of from about 0 to about 10.

A preferred gelled aqueous acid solution of this invention is comprised of an inorganic aqueous acid solution

comprising water and a water soluble inorganic acid or mixture of such acids, and a gelling agent comprised of a solution of a water soluble organic solvent and a mixture of ethoxylated fatty amines having the general formula:



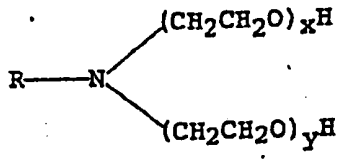
(4)

wherein:

R is selected from saturated and unsaturated aliphatic groups having in the range of from about 14 to about 18 carbon atoms and mixtures of such groups; and x and y each have a value in the range of from 0 to about 10 with the average sum of the values of x and y in the mixture being in the range of from about 1.8 to about 2.2.

The most preferred gelled aqueous acid solution of this invention is comprised of an aqueous acid solution comprising water and an inorganic water soluble acid or a mixture of such acids, and a gelling agent present in the aqueous acid solution in an amount in the range of from about 1 to about 10 percent gelling agent by weight of the acid solution. The gelling agent is comprised of a solution of a water soluble organic solvent, and a mixture of ethoxylated fatty amines present in the gelling agent in an amount of from about 10 to about 80 percent amines

by weight of the gelling agent. The ethoxylated fatty amines have the general formula:



(5)

wherein:

R is selected from the group consisting of saturated and unsaturated aliphatic groups having in the range of from about 16 to about 18 carbon atoms and mixtures of such groups; and

the average sum of the values of x and y in said mixture of ethoxylated amines is equal to 2.

In the most preferred embodiment, x and y in formula (5) each have a value of one (1).

The gelled aqueous acid solutions of this invention are stable over a wide temperature range and therefore will not chemically degrade with time, even at a temperature as high as 250°F. It must be understood, however, that the gelled acids of this invention, like other liquids, do experience viscosity change with temperature change. Thus, for example, with increasing temperature, the viscosity of these gels declines, but is regained upon decrease of temperature. Thus, gels made according to this invention have long storage life.

While the gelled aqueous acid solutions of this invention have a variety of uses, they are particularly suitable

for carrying out acid treatments in subterranean well formations for increasing the production of hydrocarbon fluids therefrom. When the gelled aqueous acid solutions are introduced into subterranean well formation, the acid spends by reacting with materials in the formation, e.g., limestone and/or dolomite, whereby salts (e.g., chlorides when HCl is used) are formed. The formation of salts in the spent acid solution causes the viscosity of the solution to decrease. That is, as the acid spends and salts form, the viscosity of the spent acid solution begins to decrease when acid concentration is in the range of about 10 to 15 percent. Thus, chemicals known in the art as "breakers" are not required when the gelled acid solutions of this invention are used to acid treat subterranean well formations. The spent acid solutions, after breaking, have viscosities in the range of from about 5 to about 15 centipoises and have excellent particle suspension properties which facilitates the efficient clean-up of a treated formation.

In using the gelled aqueous acid solutions for carrying out acidizing treatments in a subterranean well formation, an aqueous acid solution of desired acid strength is first prepared. For example, in carrying out acidizing or acid fracturing treatments in limestone or dolomite formations, aqueous hydrochloric acid solutions in concentrations in

the range of from about 3% to about 28% by weight are often utilized. After the particular aqueous acid solution to be used has been prepared and diluted to the desired strength, the gelling agent of the present invention is combined therewith, preferably in an amount in the range of from about 0.1 to about 10 percent by weight of the acid solution whereby the viscosity of the solution is increased. Other conventional well formation treating additives, such as corrosion inhibitors, non-emulsifying agents, fluid loss additives, etc., can also be combined with the solution. The resultant gelled aqueous acid solution is introduced into the formation to carry out an acidizing or acid fracturing treatment therein. After the aqueous acid solution has become spent by reaction with materials in the formation and thereby broken to a low viscosity fluid, it is produced from the formation and the formation is cleaned up using conventional clean-up procedures followed by placing the formation on production.

When a gelled aqueous hydrochloric acid solution of this invention having an initial acid concentration of below about 22 percent by weight of solution spends on limestone or dolomite to thus form calcium chloride and magnesium chloride and cools, some water and the gelling agent can separate out of the solution as a thick viscous phase. Separation does not occur when the initial hydrochloric

acid concentration is above about 22 percent by weight. In order to prevent separation in spent solutions when acid concentrations below about 22 percent by weight are utilized, calcium chloride can be added to the aqueous hydrochloric acid solution prior to gelling in an amount such that after reaction, the spent solution contains a calcium chloride concentration equivalent to a spent 22 percent by weight hydrochloric acid solution. The amount of calcium chloride required generally falls within the range of from about 1 percent to about 10 percent by weight of the spent solution. That is, when a gelled aqueous hydrochloric acid solution having an acid concentration of above about 22 percent by weight of the solution is utilized in the treatment of subterranean well formations containing calcium, no calcium chloride is added to the live solution. When a gelled aqueous hydrochloric acid solution at a concentration of 20 percent by weight of solution is utilized, about 308 pounds of calcium chloride per 1000 gallons of aqueous acid solution are added thereto which prevents separation at low temperatures (150°F and below). When a gelled aqueous hydrochloric acid solution having a concentration of 15 percent by weight is utilized, about 1040 pounds of calcium chloride per 1000 gallons of acid solution are combined therewith to prevent such separation.

The following examples are given in order to further

illustrate the gelling agent and gelled aqu ous acid solutions of the present invention.

Example 1

Gelling agents of the present invention are prepared using various mixtures of ethoxylated fatty amines dissolved in glacial acetic acid. The gelling agents are added to aqueous acid solutions containing 15 percent by weight hydrochloric acid, and the viscosities of the resultant gels determined. The viscosities of the gels are apparent viscosities measured on a Model 35 FANN viscometer, no. 1 spring, standard bob and sleeve, at room temperature (72 - 76°F) and at 300 rpm. The results of these tests are given in Table I below.

TABLE I - VISCOSITIES OF GELLED AQUEOUS HYDROCHLORIC ACID SOLUTIONS USING VARIOUS GELLING AGENTS

Ethoxylated Fatty Amine Fatty Acid Origin	Average Mol s of Ethylene Oxide Per Mole of Amine	Concentration of Amines Contained in Gelling Agent, % by Weight of Acetic Acid-Amine Solution	Concentration of Gelling Agent in Hydrochloric Acid Solution, % by Weight	Viscosity of Gelled Aqueous HCl Solution, cp
Coconut (Mixture of Chains Having 8, 10, 12, 14, 16 and 18 Carbon Atoms)	2	33.3	9	3
Coconut (Mixture of Chains Having 8, 10, 12, 14, 16 and 18 Carbon Atoms)	5	33.3	9	3
Soya (Mixture of Chains Having 14, 16 and 18 Carbon Atoms)	2	33.3	9	77
Soya (Mixture of Chains Having 14, 16 and 18 Carbon Atoms)	5	33.3	9	3
Tallow (Mixture of Chains Having 14, 16 and 18 Carbon Atoms)	2	33.3	9	55
Oleyl (18 Carbon Atoms)	2	33.3	9	82
Palmityl (16 Carbon Atoms)	2	50	6	52

From Table I it can be seen that gelling agents containing ethoxylated fatty amines derived from coconut, soya, tallow, oleic, and palmitic fatty acids increase the viscosity of aqueous hydrochloric acid solutions.

The results provided in Table I also make it clear that ethoxylated fatty amines having an average of 2 moles of ethylene oxide per mole of amine and containing hydrocarbon chain lengths of 14 to 18 carbon atoms significantly increase the viscosity of aqueous hydrochloric acid solutions.

Example 2

A gelling agent is prepared by dissolving 3 grams of ethoxylated soya amines having an average of 2 moles of ethylene oxide per mole of amine in 6 mls. (about 7 grams) of glacial acetic acid. The approximate composition of a commercial mixture of fatty acids from which the soya amine is derived is as follows:

Acid	% By Weight
myristic (C_{14})	0 to 1%
palmitic (C_{16})	6 to 10%
stearic (C_{18})	2 to 4%
oleic (C_{18})	21 to 29%
linoleic (C_{18})	50 to 59%
linolenic (C_{18})	4 to 8%

The gelling agent is combined with 125 mls. (about 134 grams) of an aqueous hydrochloric acid solution containing

15 percent by weight hydrochloric acid. Aft r mixing, the aqueous hydrochloric acid solution has an apparent viscosity of 95 centipoises measured on a Model 35 FANN viscometer, no. 1 spring, standard bob and sleeve at room temperature (72 - 76°F) and 300 rpm.

Example 3

Gelling agents are prepared by dissolving 5 grams of ethoxylated tallow amines having an average ethylene oxide content of 2 moles per mole of amine with various organic solvents. The gelling agents are then each added in amounts of 10 mls. to 200 mls. of an aqueous acid solution prepared by combining 126.8 mls. of tap water with 73.2 mls. of a hydrochloric acid solution containing 37.5 percent by weight hydrochloric acid to thus produce 200 mls. of 15 percent HCl solution which weighed 215 grams. The solution also contains 25 grams of calcium chloride and 0.4 ml. of a hydrochloric acid corrosion inhibitor. After mixing the gelling agents with the acid solutions, the apparent viscosities of the resulting gelled aqueous hydrochloric acid solutions are determined using a Model 35 FANN viscometer, no. 1 spring, standard bob and sleeve at 80°F and 300 rpm. The results of these tests are shown in Table II below.

TABLE II - VISCOSITIES OF GELLED AQUEOUS HYDROCHLORIC ACID SOLUTIONS USING GELLING AGENTS CONTAINING VARIOUS ORGANIC ACIDS

Quantity of Ethoxylated Tallow Amines, ml (grams)	Organic Solvent	Quantity of Organic Solvent, ml (grams)	Degree of Difficulty in Dissolving Amines in Solvent Used	Viscosity of Gelled Aqueous Hydrochloric Acid solutions
5 (5)	Propionic acid	5 (5.0)	Easily dissolved	51
5 (5)	Acetic acid	5 (5.2)	Very easily dissolved	70
5 (5)	Formic Acid - 88%	5 (5.9)	Difficult	88
5 (5)	Acetone	5 (3.9)	Easily dissolved	67
5 (5)	Ethylene Glycol	5 (5.5)	Easily dissolved	75

Example 4

Gelling agents are prepared by dissolving ethoxylated tallow amines having an average of 2 moles of ethylene oxide per mole of amine in various organic acids in amounts of 50 percent by weight of amine-acid solution. Each of the gelling agents are combined with aqueous hydrochloric acid solutions in amounts of 5 percent gelling agent by weight of the acid solutions, and the viscosities of the resulting gelled aqueous acid solutions are determined at various temperatures. Each of the aqueous acid solutions contain 15 percent hydrochloric acid by weight, 12.5 grams of calcium chloride per 100 cc of acid solution, and 0.2 percent by weight of a hydrochloric acid corrosion inhibitor.

TABLE III - VISCOSITIES OF GELLED HYDROCHLORIC ACID SOLUTIONS AT VARIOUS TEMPERATUES USING GELLING AGENTS CONTAINING VARIOUS ORGANIC ACIDS

Organic Acid	Viscosities of Gelled Aqueous HCl Solutions, cp									
	90°F	100°F	110°F	120°F	130°F	140°F	150°F	160°F	170°F	180°F
Formic	70	66	61	55	48.5	40	30	23.5	19	16
Acetic	67	61	54	46	35	29	23	19	14.5	10.5
Propionic	41.5	30	21.5	16	13	10.5	8	6	4.5	3.5

As illustrated in Tables II and III above, gelling agents wherein formic acid is used as the amine solvent achieve the highest apparent viscosity in hydrochloric acid solutions. However, because the dissolution of ethoxylated fatty amines in formic acid is difficult, acetic acid is preferred for use in accordance with this invention.

Example 5

A gelling agent is prepared by dissolving ethoxylated tallow amines having an average ethylene oxide content of 2 moles per mole of amine in acetic acid in an amount of 50 percent by weight of the amine-acid solution. Various amounts of the gelling agent are combined with aqueous hydrochloric acid solutions containing 15 percent by weight hydrochloric acid and 0.4 percent by weight hydrochloric acid corrosion inhibitor. The apparent viscosities of the resulting gelled aqueous hydrochloric acid solutions are determined at various temperatures using a Model 35 FANN viscometer, no. 1

spring, standard bob and sleeve at 300 rpm. The results of these tests are given in Table IV b low.

TABLE IV - VISCOSITIES OF GELLED AQUEOUS HYDROCHLORIC ACID SOLUTIONS AT VARIOUS TEMPERATUES USING VARIOUS QUANTITIES OF GELLING AGENT

Percent Gelling Agent By Weight of Acid Solution	Viscosities of Gelled Aqueous HCl Solutions, cp							
	90°F	100°F	110°F	120°F	130°F	140°F	150°F	160°F
2	19	8.5	4	3	2.5	--	--	--
3	37.5	35	31.5	27	21	15.5	6	2.5
4	48.5	45	40	31.5	24	18	14	10
5	68.5	65	50	38	31	24	19	14

From Table IV it can be seen that by increasing the amount of gelling agent combined with an aqueous solution, the viscosity of the resultant gelled solution is increased.

Example 6

A gelling agent is prepared by dissolving ethoxylated tallow amines having an ethylene oxide content of 2 moles per mole of amine in glacial acetic acid in an amount of 50 percent by weight of the resulting solution. A portion of the gelling agent is combined with an aqueous hydrochloric acid solution in an amount of 5 percent by weight of the acid solution. The acid solution contains 15 percent by weight of hydrochloric acid, 12.5 grams of calcium chloride

per 100 cc of the solution and 0.2 percent by weight of a hydrochloric acid corrosion inhibitor. Th resulting gelled aqueous hydrochloric acid solution is spent to 10.3 percent by weight live hydrochloric acid by reacting the solution with limestone. Viscosities of the spent solution are determined at various temperatures using a Model 35 FANN viscometer, no. 1 spring, standard bob and sleeve at 300 rpm. The results of these tests are given in Table V.

TABLE V - VISCOSITIES OF GELLED 15% BY WEIGHT AQUEOUS HYDROCHLORIC ACID SOLUTION AT VARIOUS TEMPERATURES AFTER BEING SPENT TO 10.3% BY WEIGHT LIVE ACID

Temperature, °F	Viscosity, cp
84	70
90	45
100	7
110	5
120	3.5
130	2

From Table V it can be seen that when a gelled 15 percent by weight hydrochloric acid solution is spent to a live acid concentration of 10.3 percent by weight, the acid solution is broken to a viscosity of less than about 10 cp at a temperature of 100°F.

Example 7

A gelling agent is prepar d as described in Example 6 and is combined with an aqueous hydrochloric acid solution in an amount of 5 percent by weight of acid solution. The hydrochloric acid solution contains 28 percent by weight hydrochloric acid and 0.5 percent by weight acid corrosion inhibitor. The resulting gelled aqueous hydrochloric acid solution is spent by reaction with limestone to various live acid concentrations, and the viscosities of such partially spent solutions are determined at various temperatures using a Model 35 FANN viscometer, no. 1 spring, standard bob and sleeve at 300 rpm. The results of these tests are shown in Table VI below.

TABLE VI - VISCOSITIES OF GELLED 28% BY WEIGHT AQUEOUS HYDROCHLORIC ACID SOLUTIONS AT VARIOUS TEMPERATURES AFTER BEING SPENT TO VARIOUS LIVE ACID CONCENTRATIONS

Spent Solution Live Acid Concentration, % By Weight	Viscosities of Spent Acid Solutions, cp							
	90°F	100°F	110°F	120°F	130°F	140°F	150°F	160°F
19.9	19.5	20	20	19	18	16.5	15	13
15.9	70	66.5	60	51	40	30	5	3
10.3	45	8.5	6	5	4	3	2	1.5
6.2	6	---	---	---	---	---	---	---

From Table VI it can be seen that when a gelled aqueous hydrochloric acid solution of this invention containing 28

percent by weight hydrochloric acid is spent to a live acid concentration below about 16 percent by weight, such spent solution is broken to a viscosity below about 5 cp at 150°F.

Example 8

A gelling agent of the present invention is prepared by dissolving ethoxylated tallow amines having an ethylene oxide content of 2 moles per mole of amine in glacial acetic acid in an amount of 50 percent by weight of the solution. Portions of the gelling agent are added to aqueous hydrochloric acid solutions, and the resulting gelled hydrochloric acid solutions are spent by reaction with limestone. The apparent viscosities of the spent solutions are measured on a Model 35 FANN viscometer, no. 1 spring, standard bob and sleeve at 300 rpm. the particle or fines suspending properties of the spent acid solutions are determined by placing 2 grams of fines in 100 ml portions of the spent solutions, mixing the solutions and then allowing the fines to settle in the solutions for 6 hours. The fines remaining suspended in the solutions after the 6-hour periods are determined by collecting the fines by centrifugation, washing, drying and weighing. The results of these tests are given in Table VII below.

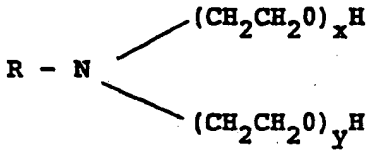
TABLE VII - FINE SUSPENSION ABILITY OF SPENT GELLED AQUEOUS ACID SOLUTIONS

Gelled Aqueous Acid Solution				Solution Live Acid Concentration After Spending, % HCl By Weight	Viscosity Of Spent Acid After Solution, cp	Suspended Fines in Spent Acid Solution After 6 Hours, mg/100 cc
HCl, by Weight	Calcium Chloride, Grams/100 cc Acid Solution	Acid Corrosion Inhibitor, % By Weight	Gelling Agent % By Weight			
15	12.5	0.2	5	1.5	10 (74°F)	206
20	3.7	0.2	5	1.2	5 (80°F)	279
28	0	0.2	5	1.4	7.5 (64°F)	330
Deionized water only						5

From Table VI it can be seen that the spent gelled aqueous acid solutions of this invention have excellent fines suspension capability.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A gelled aqueous inorganic acid solution comprising water, at least one water soluble inorganic acid and a gelling agent, said gelling agent being comprised of a water soluble organic solvent selected from the group consisting of alkanols having in the range of from about 1 to 5 carbon atoms per molecule, ketones having in the range of about 3 to 6 carbon atoms per molecule, polyhydroxy compounds having in the range of about 2 to 6 carbon atoms per molecule, ethers having in the range of about 2 to 6 carbon atoms per molecule, compounds containing both ether and alcohol functions having in the range of about 4 to 8 carbon atoms per molecule, esters having in the range of about 2 to 6 carbon atoms per molecule, lactones having in the range of about 3 to 5 carbon atoms per molecule and mixtures of two or more of the foregoing compounds, and a mixture of ethoxylated fatty amines dissolved in said water soluble organic solvent having the general formula:



wherein:

R is selected from saturated and unsaturated aliphatic groups having in the range of from about 8 to about 22 carbon atoms and mixtures thereof, and

x and y each have a value in the range of from 0 to about 10.

2. The gelled aqueous inorganic acid solution of claim 1 wherein the average sum of the values of x and y in said mixture of ethoxylated fatty amines is in the range of from about 1.8 to about 2.2.

3. The gelled aqueous inorganic acid solution of claim 2 wherein said gelling agent is present in said acid solution in an amount in the range of from about 0.1% to about 10% gelling agent by weight of said acid solution.

4. The gelled aqueous inorganic acid solution of claim 3 wherein R is selected from the group consisting of saturated and unsaturated aliphatic groups having in the range of from about 16 to about 18 carbon atoms and mixtures thereof, and wherein the average sum of the values of x and y in said mixture of ethoxylated fatty amines is equal to 2.

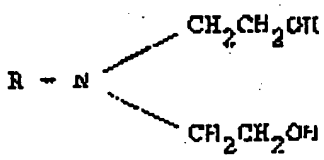
5. The gelled aqueous inorganic acid solution of claim 2 wherein said ethoxylated fatty amines are present in said gelling agent in an amount in the range of from about 10% to about 80% by weight of said gelling agent.

6. The gelled aqueous inorganic acid solution of claim 4 wherein said water soluble organic solvent is an alkanol selected from the group consisting of methanol, ethanol, isopropanol, t-butanol and mixtures thereof, and said ethyoxylated fatty amines are present in said gelling agent in an amount of about 50% by weight of said gelling agent.

7. The gelled aqueous inorganic acid solution of claim 2 wherein said water soluble inorganic acid is hydrochloric acid.

8. A gelled aqueous inorganic acid solution comprising water, an inorganic acid and a gelling agent, said gelling

agent being comprised of a water soluble organic solvent selected from the group consisting of alkanols having in the range of from about 1 to 5 carbon atoms per molecule, ketones having in the range of about 3 to 6 carbon atoms per molecule, polyhydroxy compounds having in the range of about 2 to 6 carbon atoms per molecule, ethers having in the range of about 2 to 6 carbon atoms per molecule, compounds containing both ether and alcohol functions having in the range of about 4 to 8 carbon atoms per molecule, esters having in the range of about 2 to 6 carbon atoms per molecule, lactones having in the range of about 3 to 5 carbon atoms per molecule and mixtures of two or more of the foregoing compounds, and an ethoxylated fatty amine dissolved in said water soluble organic solvent having the general formula:



Wherein:

R is selected from the group consisting of saturated and unsaturated aliphatic groups and mixtures thereof having in the range of from about 14 to about 18 carbon atoms.

9. The gelled aqueous inorganic acid solution of claim 8 wherein R is selected from the group consisting of saturated and unsaturated aliphatic groups and mixtures thereof having in the range of from about 16 to about 18 carbon atoms.

10. The gelled aqueous inorganic acid solution of claim 9 wherein said water soluble organic solvent is an alkanol selected from the group consisting of methanol, ethanol, isopropanol, t-butanol and mixtures thereof.

11. The gelled aqueous inorganic acid solution of claim 9 wherein said ethoxylated fatty amine is present in said gelling agent in an amount in the range of from about 10% to about 80% by weight of said gelling agent.

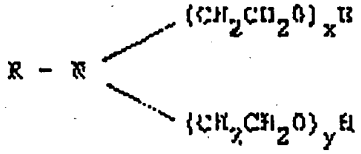
12. The gelled aqueous inorganic acid solution of claim 9 wherein said water soluble inorganic solvent is methanol and said ethoxylated fatty amine is present in said gelling agent in an amount of about 50% by weight of said gelling agent.

13. The gelled aqueous inorganic acid solution of claim 12 wherein said gelling agent is present in said acid solution in an amount in the range of from about 0.1% to about 10% by weight of said acid solution.

14. A method of treating a subterranean well formation comprising the steps of:

combining a gelling agent with an aqueous inorganic acid solution in an amount in the range of from about 0.1% to about 10% by weight of said solution whereby the viscosity of said solution is increased, said gelling agent being comprised of a water soluble organic solvent selected from the group consisting of alkanols having in the range of from about 1 to 5 carbon atoms per molecule, ketones having in the range of about 3 to 6 carbon atoms per molecule, polyhydroxy compounds having in the range of about 2 to 6 carbon atoms per molecule, ethers having in the range of about 2 to 6 carbon atoms per molecule, compounds containing both ether and alcohol functions having in the range of about 4 to 8 carbon atoms per molecule, esters having in the range of about 2 to 6 carbon atoms per molecule, lactones having in the range of about 3 to 5 carbon atoms per molecule and mixtures of two

or more of the foregoing compounds, and a mixture of ethoxylated fatty amines dissolved in said water soluble organic solvent having the general formula:



wherein:

R is selected from saturated and unsaturated aliphatic groups having in the range of from about 8 to about 22 carbon atoms and mixtures thereof and

x and y each have a value in the range of from 0 to about 10 with the average sum of the values of x and y in said mixture being in the range of from about 1.8 to about 2.2; and

introducing said solution into said subterranean formation.

15. The method of claim 14 wherein R is selected from the group consisting of saturated and unsaturated aliphatic groups having in the range of from about 14 to about 18 carbon atoms and mixtures thereof, and wherein the average sum of the values of x and y in said mixture of ethoxylated fatty amines is equal to 2.

16. The method of claim 15 wherein said ethoxylated fatty amines are present in said gelling agent in an amount in the range of from about 10% to about 00% by weight of said gelling agent.

17. The method of claim 16 wherein said water soluble organic solvent is an alkanol selected from the group consisting of methanol, ethanol, isopropanol, t-butanol and mixtures thereof and said ethoxylated fatty amine is present in said gelling agent in an amount of about 50% by weight of said gelling agent.

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18. The method of claim 14 wherein said inorganic acid is hydrochloric acid.

19. The method of claim 14 wherein said aqueous inorganic acid solution is an aqueous hydrochloric acid solution having a hydrochloric acid concentration of above about 22% by weight of said solution.

20. The method of claim 15 wherein said aqueous inorganic acid solution is an aqueous hydrochloric acid solution having a hydrochloric acid concentration of below about 22% by weight of said solution.

21. The method of claim 20 which is further characterized to include the step of combining calcium chloride with said aqueous hydrochloric acid solution in an amount in the range of from about 1% to about 10% by weight of said solution.